BIODIESEL PRODUCTION FROM RUBBER SEED OIL USING ACTIVATED CLINKER AS CATALYST

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ABSTRACT

This study uses clinker from the cement industry as a catalyst for transesterification of rubber seed oil to biodiesel. Clinker is nodules that are obtained from sintering limestone and aluminosilicate. Accordingly, there is a need to overcome depletion of fossil fuel, fluctuating price of edible oil which is used as biodiesel feedstock and expensive noble metals. The immediate objective of this research project is to synthesize catalyst from clinker for biodiesel production and to elucidate the mechanism of catalyst activation of the cement waste. Rubber seeds were collected, dried and shelled from the kernels. Microwave extraction was used to extract the rubber seed oil using hexane as the extraction solvent. Density of rubber seed oil was determined using density meter, calorific value using bomb calorimeter, acid test using potentiometer, FFA content and fatty acid methyl ester content using gas chromatography; all the test complied with ASTM D1480, D240, D664 and D 1983 for GC. Clinker collected from the conveyer belt was crushed using the jaw crusher to obtain clinker size of below 5mm. Crushed clinker was then grinded using mortar and pestle and was passed through 200 μm sieve. Mineral composition was analysed using XRF and surface area of clinker was found using Blaine apparatus. SEM analysis was done to study the activation and concluded the optimum activation parameter morphologically for transesterification. Clinker was activated at 64.7 °C under reflux for 1 hour with catalyst methanol ratio of 1:400 using catalyst loading determined through acid test of rubber seed oil with constant stirring at 400 rpm. Reaction was done under reflux at methanol boiling point, 60 ± 0.5 °C with constant stirring for 1 hour. After reaction, the reaction mixture was allowed to settle in a separating funnel overnight. The top layer (fatty acid methyl ester) was pipette out followed by the second layer (glycerol). The top layer was washed 3 times with distilled water to remove methanol and impurities. GC analysis was done for fatty acid methyl ester. Clinker was found to contain 66.61% of CaO and 2.7% free lime. Surface area is found to be 0.56 m^2/g and acid number of FFA is 1.7952 mg KOH/g. Calorific value and density of FAME is 38.87 mJ/kg and 0.8548 g/cm^3. The entire test done to date supports the use of clinker as a novel catalyst to produce biodiesel.

ABSTRAK

Kajian ini menggunakan klinker daripada industri simen sebagai pemangkin dalam proses pembuatan biodiesel daripada minyak biji getah. Klinker adalah nodul yang diperolehi daripada pensinteran batu kapur dan aluminosilikat. Sehubungan dengan itu, adalah perlu untuk mengatasi masalah sumber bahan api fosil sedang menyusut serta harga minnyak masak yang digunakan sebagai bahan mentah biodiesel dan logam yang semakin meningkat. Objektif projek penyelidikan ini adalah untuk mensintesis pemangkin daripada klinker bagi pengeluaran biodiesel dan untuk menjelaskan mekanisme pengaktifan pemangkin sisa simen. Biji getah telah dikumpulkan, dikeringkan dan dibuang kulit dari biji. Pengekstrakan gelombang mikro digunakan untuk mengekstrak minyak biji getah menggunakan heksana sebagai pelarut pengeskstrakan. Ketumpatan minyak biji getah adalah ditentukan dengan menggunakan meter ketumpatan, nilai kalori menggunakan meter kalori bom, ujian asid menggunakan potensiometer, kandungan FFA dan kandungan metil ester asid lemak dengan menggunakan kromatografi gas; semua ujian mematuhi ASTM D1480, D240, D664 dan D1983 untuk GC . Klinker yang dikumpul dari "conveyer belt" dihancurkan menggunakan penghancur rahang untuk mendapatkan saiz klinker di bawah 5mm. Klinker yang telah dihancurkan kemudiannya dikisar menggunakan lesung dan alu dan telah dilalukan melalui ayak 200 µm. Komposisi mineral dianalisa menggunakan XRF dan permukaan kawasan klinker didapati menggunakan radas Blaine. SEM analisis telah dilakukan untuk mengkaji pengaktifan dan untuk membuat kesimpulan parameter pengaktifan optimum morfologi untuk transesterification. Klinker telah diaktifkan pada 64,7 °C di bawah refluks selama 1 jam dengan nisbah metanol pemangkin 1:400 pemangkin loading yang ditentukan melalui ujian asid minyak biji getah dengan mengacau larutan pada kadar tetap; 400 rpm. Tindak balas telah dilakukan di bawah refluks pada suhu 60 ± 0.5 °C dengan mengacau berterusan selama 1 jam. Selepas tindak balas, campuran tindak balas dibiarkan semalama. Lapisan atas (metil ester asid lemak) dipipet keluar diikuti oleh lapisan kedua (gliserol). Lapisan atas dicuci 3 kali dengan air suling untuk mengeluarkan sisa metanol berlebihan dan kotoran. Analisis GC telah dilakukan untuk menentukan komposisi metil ester asid lemak. Klinker didapati mengandungi 66,61 % CaO dan 2.7 % kapur. Luas permukaan didapati 0.56 m^2/g dan nombor asid FFA 1.7952 mg KOH/g. Nilai kalori dan ketumpatan FAME adalah 38.87 mJ/kg dan 0.8548 g/cm3 masing-masing. Keseluruhan ujian yang dilakukan setakat ini menyokong penggunaan klinker sebagai pemangkin novel untuk menghasilkan biodiesel.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

%	Percentage
°C	Degree celsius
min	Minute
µm	Micrometer
vol. %	Volume percentage
cm	Centimeter
W	Watt
g	gram
m	Metre
s	Second
ha/yr	hectare per year
ha	hectare
K	Kelvin
mm^2/s	milimeter square per second
kJ/kg	Kilo Joule per kilogram
meq/kg	miliequivalent per litre
wt %	weight per cent
ml	millilitre
ml/min	millilitre per minute

LIST OF ABBREVIATIONS

FAME	Fatty Acid Methyl Ester
FFA	Free Fatty acid
TG	Triglycerides
RSO	Rubber Seed Oil
CLK	Clinker
ASTM	American Society for Testing and Material
LHV	Lower Heating Value
XRF	X-ray fluorescence

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

The current motivation towards the production of biodiesel is the conservation of fossil fuels as well as concerns over environmental problems. Considerable attention and effort has been given in producing alternative renewable energy like biodiesel which is also known as Fatty Acid Methyl Ester (FAME) (Canakci, 2006). FAME is an alternative biofuel produced through transesterification of triglycerides (TGs) or the esterification of Free Fatty Acids (FFAs) with methanol (Meher et al., 2006). Besides that, biodiesel possesses all the favourable characteristics of diesel and is renewable, biodegradable, non toxic and 'carbon neutral' since no net amount of carbon is released to the atmosphere.

Biodiesel also has cetane number of 100 which is 60% more than in diesel. This parameter shows that biodiesel will allow cold starts and less idle noise (Lotero et al., 2005). According to Ramadhas et al. (2004), biodiesel have no sulphur content, no storage difficulties and have good lubricating properties According to Dorado and Loperz (2006), vegetable oils and fats are the main feedstock for biodiesel and an economical supply that is sustainable is a crucial factor.

Ramadhas et al. (2004) further elaborated that vegetable oils are a promising alternative to fossil fuel as they are renewable and nature friendly because they help to decrease carbon content in atmosphere. Many researchers used edible oils for example sunflower and corn to produce biodiesel but the fluctuating prices of edible oils and increasing demands for nutritional needs have made rubber seed oil to be the raw material of choice (Yusup and Khan, 2010). Biodiesel production from edible vegetable oils and animal fats as feedstock creates a big concern over the competition in the food supply. In order to overcome these issues, there is a dire need to produce biodiesel using second generation vegetable oil and the use of catalyst that reduces energy requirement in transesterification as well as cost effective.

Current biodiesel production technology uses noble metal as catalyst. Besides that, it is cannot be recycled and production cost is high due to it. Separation also becomes another problem as purification of biodiesel becomes difficult.

This research is about the production of biodiesel from rubber seed oil (RSO) using activated cement clinker as the catalyst in transesterification process.

1.2 STATEMENT OF PROBLEMS

According to Issanyakul and Dalai (2010), first generation biodiesel was produced from edible oils and the second generation biodiesel was produced from non-edible oils. The use of edible oil is seen as not being feasible according to their research. Following are the problems that have been identified with biodiesel production previously.

1.2.1 Depletion of Fossil Fuel and Degradation of Environmental Quality

Major part of energy source comes from the non-renewable fossil fuel which also pollutes the environment significantly (Sharma and Singh, 2010). Besides that, price of fossil fuel is also rocketing as the demand is higher than supply itself.

1.2.2 Fluctuating Prices of Edible Oils and Expensive Noble Metal

The use of edible oils is no longer feasible as demand for nutrition predominate the need for energy. Their availability is a concern thus prices of edible oils increases (Sarin et al., 2009). Lin et al. (2009) has stated that noble metal catalyst used in transesterification is expensive. Most of the catalyst used is non-recyclable. This causes the price of biodiesel to increase.

1.3 RESEARCH OBJECTIVES

The sole objective of this research is to produce biodiesel from rubber seed oil using catalyst derived from cement industry. Activation and characterisation of cement clinker (CLK) will be done to test its suitability as heterogeneous catalyst.

1.4 SCOPE OF STUDY

The following are the scope of study of this research:

1.4.1 Extraction of Rubber Seed Oil (RSO) From Kernels Using Soxhlet Extraction and Microwave Extraction.

1.4.2 Characterisation of Extracted RSO Using ASTM Standards.

1.4.3 Activation and Characterisation of Cement Clinker.

1.4.4 Transesterification of RSO with Activated Cement Clinker to Produce Methyl Ester (Biodiesel). Optimum Catalyst Loading Will Be Tested As Part Of Kinetic Studies.

1.4.5 Biodiesel Analysis Using ASTM Standards And Comparing With Values Of Other Feedstock.

1.5 EXPECTED OUTCOMES

It is expected that by using activated cement clinker as catalyst, a high yield of FAME can be obtained within the shortest period of transesterification reaction time of 1 hour with an acceptable biodiesel characterisation within the specifications of ASTM D 6751 for B100.

1.6 SIGNIFICANCE OF STUDY

Below are the significance of this research in terms of its novelty, applicability and commercialization.

1.6.1 Novelty of Biodiesel Production from Rubber Seed Oil

First generation feedstock used edible vegetable oil. Using crops for energy and food compete with each other in many ways (agricultural land, skilled labours, water, fertilizers, etc.). Using second generation feedstock which is non- edible vegetable oil will be more feasible. Besides that, activated cement clinker will be used as a catalyst instead of the expensive noble metals.

1.6.2 Applicability of This Study

Use of rubber seeds and cement clinker is a great opportunity to convert waste to wealth and recycling of catalyst for cost efficient biodiesel production.

1.6.3 Commercialisation

According to statistics done by KDPN HEP, annual consumption of diesel in Malaysia in year 2010 was 11.655 billion litres. Annual revenue of RM 340.082 billion can be generated if biodiesel from rubber seed oil is sold at RM 2.581 per litre (Biofuel Database in East Asia), the current price in 2011 for fossil diesel.

1.7 CONCLUSION

It is hoped that biodiesel can be produced from rubber seed oil using activated clinker as the catalyst for transesterification using the scope outlines and the amount of FFA in crude oil can be reduced.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This section will discuss the reviews on biodiesel production from rubber seed oil using activated clinker as catalyst. This review will be divided into; (a) depletion of fossil fuel and introduction to biodiesel, (b) types of feedstock available and selection of feedstock, (c) types of catalyst and selection of catalyst and (d) methods to produce biodiesel.

2.2 Depletion of Fossil Fuel and Introduction to Biodiesel

As a result of the birth of industrial revolution in the late 18^{th} and early 19^{th}, energy has become a crucial reason for human to protect economic growth and maintain standard of living. The extension of industrial revolution in Europe had been largely contributed by the abundant availability and accessibility of coal as the primary source of energy. On the other hand, the arrival of automobiles, airplanes and electricity had been made possible by the energy use of petroleum in the 20^{th} century. Marked to this date, energy has been continuously obtained from conventional sources (fossil fuels).

Currently, we are facing problems like depletion of fossil fuel, increasing demands for diesels and uncertainty in the availability of fossil fuel (Singh and Singh, 2010). There is excess use of fossil fuel and it is predicted that in another 80 years, mankind will face huge problems. Fossil fuels take millions of year to form from bacteria activities from beneath the sea levels.

According to Shay (1993), Rudolf Diesel first tested the use of vegetable oil in particular, peanut oil as fuel for his engine about 120 years ago. The usage of this biofuel continued until 1920s before petroleum-derived diesel almost completely vanished vegetable oils in the market because of its lower price, higher availability and government subsidies.

Biodiesel is an initiative alternative source of energy that is being produced to overcome fossil fuel depletion. This can be seen from the effort that had been started over a century ago. Alternative fuel has been accepted as early 1982 by holding the first international conference on plant and vegetable oils as fuels (Singh and Singh, 2010). Even in Kyoto Protocol, the use of biodiesel throughout the world has been advised. The European Community in 1991 has proposed a tax reduction of 90% for the use of biofuels including biodiesel (Haque et al., 2009).

Biodiesel is beneficial as it is renewable, biodegradable, non-toxic and aromatic. It is also sulphur free and has potential in reducing levels of pollutants and probable carcinogens (Martini and Shell, 1998). Due to having better properties than that of petroleum diesel itself, it can be concluded that the search for biodiesel is indeed beneficial to mankind as it has many advantages as a substituent.

2.3 Types of Feedstock Available and Selection of Feedstock

There are various types of suitable raw materials for biodiesel production. There are many types of vegetable oil and animal fats that can be used as raw materials in biodiesel production (Lee et al., 1995). The feedstock for biodiesel can vary from one country to another country depending on their geographical locations and agricultural trend (Bryan, 2009). Most of the raw materials used are first generation feedstocks which are edible. Edible feedstock should not be used as it will not be cost effective and it is not feasible to be used in a larger scale. If this issue is viewed in countries with large population like India and China, there is a large gap between the demand for fuel and supply provided (Singh and Singh, 2010). There will be fight over for sustainability and food for fuel production. In India, only plants that are non-edible which can produce oil in an acceptable quantity and that can be grown on large scale on non- cropped marginal and waste lands can be used. A list of biodiesel feedstock in the form of vegetable oils, non-edible oils, animal fats and some other biomass are listed in Table 2.1.

Table 2.1: List of biodiesel feedstock

Vegetable oils	Non-edible oils	Animal fats	Other sources
Soybeans	Almond	Lard	Bacteria
Rapeseed	*Abutilon muticum*	Tallow	Algae
Canola	Andiroba	Poultry fat	Fungi
Safflower	Babassu	Fish oil	Micro algae
Barley	*Brassica carinata*		Tapenes
Coconut	*B. napus*		Latexes
Copra	Camelina		Cooking oil
Cotton seed	Cumaru		(Yellow grease)
Groundnut	*Cynara*		Microalgae
Oat	*cardunculus*		(Chlorellavulgaris)
Rice	Jatrophacurcas		
Sorghum	*Jatropha nana*		
Wheat	Jojoba oil		
Winter rapeseed oil	Pongamiaglabra		
	Laurel		
	Lesquerellafendleri		
	Mahua		
	Piqui		
	Palm		
	Karang		
	Tobacco seed		
	Rubber plant		
	Rice bran		
	Sesame		
	Salmon oil		

Source: Singh and Singh (2010)

As seen in Table 2.1, there are many concerns regarding the use of vegetable oils in terms of its applicability and also the cost of biodiesel. The price of vegetable oil is high and therefore using it will not be cost effective (Singh and Singh, 2009). Selecting the best feedstock is important to make sure of low biodiesel production cost. Feedstock supply and price alone contributes to 75% of the overall production (Meng et al., 2009). To ensure that biodiesel remain comparable to petroleum-derived diesel, feedstock should be accessible at the lowest price possible and abundantly available. Using wheat and rice as biodiesel feedstock will definitely not be feasible as it the staple food in most countries. Ramadhas et al. (2005) revealed that vegetable oils have no sulphur content, offer no storage difficulty, have excellent lubricating properties, absorb more carbon dioxide and will definitely help to reduce carbon dioxide content in atmosphere.

Of all the available feedstock, Yusup and Khan (2010) suggest that rubber seeds are underutilised and have no major application in industry. Rubber seeds are also easily available in Malaysia (Yusup and Khan, 2010). Based on research done by Eka et al. (2010), there were estimated acreage of 1, 229, 940 hectares of rubber plantation in 2007. An estimated average of 1000 kg seeds per ha/ yr are produced. Rubber trees cover more than 1.2 million ha all over the country (Malaysian Rubber Board Statistics, 2009). Each hectare can give approximately 150 kg of seeds. Rubber seed kernels (50-60 % of seed) contain 40-50% of brown colour oil (Ramadhas et al., 2005). Ramadhas et al. further characterised rubber seeds stating that they are ellipsoidal, variable in size, 2.5-3 cm long, mottled brown, lustrous, weighing 2-4 g each.

2.4 Rubber Seed Oil and Fuel Characterisation

The establishment and commercialisation of biodiesel in many countries around the world has triggered the development of standards to ensure and promise high quality of product and user confidence. Two of the widely used biodiesel standards are ASTM D6751 (ASTM = American Society for Testing and Materials) and the European standard EN14214. Biodiesel is characterised by determining its physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pure point, gross heat of combustion and volatility. In conclusion, biodiesel compares well to petroleum-based diesel

The benefits offered by biodiesel outweigh that of diesel itself. According to Demirbas (2009), “The advantages of biodiesel as diesel fuel are its portability, ready availability, renewability, higher combustion efficiency, lower sulphur and aromatic content, higher cetane number and higher biodegradability”. The obvious disadvantages of biodiesel as diesel fuel on the other hand are its higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxide emission, lower engine speed and power, injector coking, engine compatibility, high price, and higher engine wear as stated by Demirbas (2008).

There are more safety benefits offered by biodiesel compared to diesel fuel as it is much less combustible, with a flash point greater than 423 K compared to 350 K for petroleum-based diesel fuel (Demirbas and Balat, 2006). Biodiesel has a higher cetane number (around 50) than diesel fuel (Balat and Balat, 2008). Cetane number is used as indicator to determine diesel fuel quality, especially the ignition quality. It is to measure the readiness of the fuel to auto-ignite when injected into the engine. Ignition quality is determined by the structure of the fatty acid methyl ester (FAME) component (Bamgboye and Hansel, 2008). Viscosity is a very vital property of biodiesel since it affects the operation of the fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. Biodiesel has viscosity which is close to that of diesel fuels. High viscosity causes poorer atomization of the fuel spray and less accurate operation of the fuel injectors (Balat, 2008). Due to presence of electronegative element oxygen, biodiesel is slightly more polar than diesel fuel as a result viscosity of biodiesel is higher than diesel fuel. Presence of elemental oxygen lowers the heating value of biodiesel when compared the diesel fuel (Kulkarni et al., 2008). The lower heating value (LHV) is the most common value used for engine applications. It is used as an indicator of the energy content of the fuel. Biodiesel generally has a LHV that is 12 % less than because of its environmental benefits and the fact that it is made from renewable resources.

The properties biodiesel in comparison with standard biodiesel and diesel (Table 2.2) can be observed.

Table 2.2: Shows properties of rubber seed oil in comparison with diesel

Property	Test procedures	Rubber seed oil	Diesel
Specific gravity	ASTM D4052	0.91	0.835
Viscosity (mm^2/s)	ASTM D445	76.4	7.50
Flash point (°C)	ASTM D93	198	50
Calorific value (kJ/kg)	ASTM D240	37 500	42 250
Iodine value	-	135.3	38.3
Acid value	ASTM D974	53.0	0.062

Source: Ramadhas et al. (2005)

If seen in the above table, the acid value of crude rubber seed oil is critically high if compared to diesel's acid value. Khan et al. (2010) has clearly stated using crude non-edible oils and fats contribute to high free fatty acid (FFA) content.

For instance, the rubber seed oil extracted in Jose et al. (2011)'s study shows that it contains 35 mg KOH/g, which is equivalent to 17.5 % FFA. High FFA contents prevent single step transesterification using base catalyst because saponification takes place and forms soap. This will harden the separation process of ester and glycerol (Ikwuagwu et al., 2000). Yusup and Khan (2010) reported that using refined and bleached rubber seed oil before running the experiment lowers the acid value but at the same time they agreed that refining will add cost to the process. Jose et al. (2011) also related high FFA with high viscosity of oil. Besides that, acid esterification is also widely used to treat high fatty acid crude rubber seed oil (Khan et al., 2010).

Table 2.3: Physiochemical properties of crude oil and refined (bleached) rubber seed oil

Analysis	Crude rubber seed oil	Refined rubber seed oil
Physical state at 30 °C	Liquid	Liquid
Colour	Golden yellow	Golden yellow
Specific gravity at 30 °C	0.922	0.918
Refractive index at 40 °C	1.4654	1.4650
Viscosity (cSt) at 30 °C	41.24	37.85
Smoke point (°C)	245	244
Flash point (°C)	294	290
Fire point (°C)	345	345
Acid value	4.0	1.0
Free fatty acid (as oleic)	2.0	0.5
Peroxide value (meq/kg)	2.5	1.0
Iodine value	142.6	142.6
Saponification value	194.0	185.8
Unsaponifiable matter	1.18	0.16

Source: Ikwuagwu et al. (2000)

Table 2.4: Yields of ester-fuel (weight per cent)

	% Yield of ester at 30 °C	% Yield of glycerol
Crude oil	76.64	13.98
Refined (bleached) oil	84.46	8.79

Source: Ikwuagwu et al. (2000)

It can be seen obviously that after refining the crude oil, the yield of ester increases. Therefore, to get a higher product, crude oil need to be refined to bring down acid value, eliminate the chances of saponification and increase product yield. Added cost for refining is inevitable but it will be cut off with the product sales.

Table 2.5: Properties biodiesel in comparison with standard biodiesel and diesel

Property	Test procedure	Biodiesel-Standard ASTM D6751-02	Rubber seed oil-biodiesel	Diesel
Specific gravity at 30 °C	ASTM D4052	0.87-0.90	0.837	0.839
Kinematic Viscosity at 40 °C (mm^2/s)	ASTM D445	1.9-6.0	3.12	3.18
Heating value (kJ/kg)	ASTM D240	-	38.20	42
Flash point (°C)	ASTM D93	Max 130	128	68
Cloud point (°C)	ASTM D2500	-3 to 12	5	17
Pour point (°C)	ASTM D97	-1.5 to 10	-7	-20
Carbon residue (%)	-	<0.3	0.14	0.17

Source: Jose et al. (2011)

The marketability of vegetable oil depends on its fatty acids and the convenience to be modified or altered with the use of other chemicals (Pryde and Rothfus, 1989). The content of fatty acids in rubber seed oil is as follows; 17-20 % saturated fatty acids (myristic, palmitic, stearic, arachidic and behenic) and 77-82 % unsaturated fatty acids (palmitoleic, oleic, linoleic, linolenic and arachidoleic) (Hardjosuwito and Hoesnan, 1978).